

# Chapter 2: Ideal Gases

- In this chapter we want to begin to explore the relationship between temperature and thermal energy and some of the microscopic properties of an object.
- We will begin by developing a model for an **ideal gas**.
  - We will define an **ideal gas** as any gas that behaves like our model.
    - ❑ This definition does not guarantee that such a gas exists.
    - ❑ However, it turns out that many gases, especially in the low density limit behave very much like the model we are about to construct, so it is a useful exercise.
- **Ideal Gas: (Assumptions)**

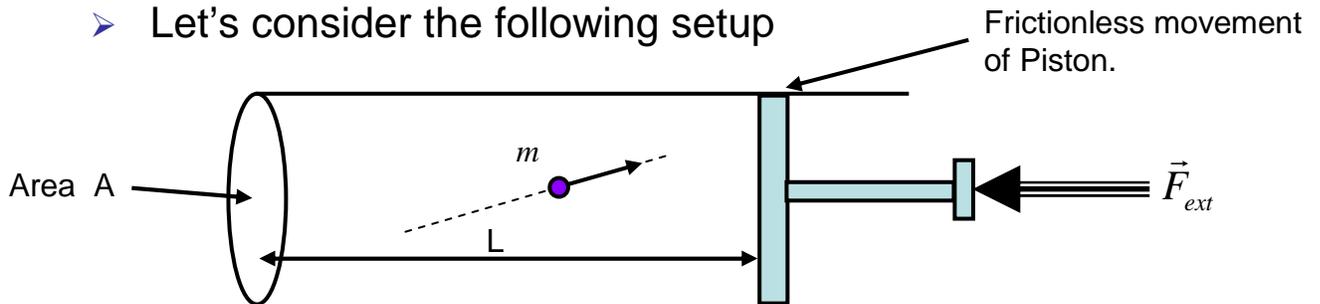


# Ideal Gas



- Now let's work with this model to understand what it predicts regarding the connection between temperature and internal energy.

- First, we assume for this model that the pressure that a gas exerts on its container must be from the molecules of the gas hitting the walls of the container and giving the wall a small impulse (momentum transfer)
- Let's consider the following setup



- The piston can move without friction. However, we are going to apply an external force that is just large enough to keep the piston in place.

# Ideal Gas Law

- Now consider a *single* gas molecule hitting the piston.
  - What is the momentum transfer?
  - The collision is elastic (ideal gas assumption)
    - 
    -
- By conservation of momentum the piston must feel an impulse:
- Now the molecule can bounce off other walls but its  $|v_x|$  will not change. So eventually the molecule will bounce off the opposite wall and head back towards the piston. The time *between* collisions with the piston will be:
- The average force that this particle exerts on the piston is

$$F_{avg} = |F_{x,avg}| = \frac{\text{impulse per collision}}{\text{time between collisions}} = \frac{2m|v_x|}{\left(\frac{2L}{|v_x|}\right)} = \frac{mv_x^2}{L}$$

- Pressure is force per unit area:

$$P_{\text{one particle}} = \frac{F_{avg}}{A} = \frac{mv_x^2}{AL} = \frac{mv_x^2}{V}$$

# Ideal Gas Law

- Now how do we extend this idea to the many molecules of gas that are flying around inside of the cylinder?
  - Since the molecules do not significantly interact with one another we have to sum up the contributions from all the molecules.
  - However, not all the particles have the same  $|v_x|$ , so we cannot just multiply by  $N$ .

- Let's perform the following sum:

$$P_{total} = \sum_{i=1}^N P_i = \sum_{i=1}^N \frac{m_i v_{i,x}^2}{V} = \frac{N}{V} \left( \frac{1}{N} \sum_{i=1}^N m_i v_{i,x}^2 \right) = \frac{N}{V} [m v_x^2]_{avg}$$

- Now recall how we defined **temperature**.

$$P \equiv CT$$

- Comparing the two equations we see that we must have

$$[m v_x^2]_{avg} = k_B T$$

- Now we can take this and substitute it back into our ideal gas relationship and we come up with the following:

$$P = \frac{N}{V} k_B T \quad \Rightarrow \quad PV = N k_B T$$

**Ideal  
Gas Law**

- Note: experimentally we find that  $k_B$  is independent of  $P$ ,  $V$ ,  $N$ , and  $T$  (it's a constant)

$$k_B = 1.38 \times 10^{-23} \text{ J/K}$$

Boltzmann Constant

# Temperature and Energy

- We have seen from this last derivation that there is a connection between the temperature of an ideal gas and the average  $m|v_x^2|$ .
- Let's follow this thread. First, the x-direction is irrelevant since we could have setup the piston in the y direction or the z direction. Therefore:

$$\left[ m v_x^2 \right]_{avg} = \left[ m v_y^2 \right]_{avg} = \left[ m v_z^2 \right]_{avg} = k_B T$$

- Let's sum up each of these terms:

$$\begin{aligned} & \left[ m v_x^2 \right]_{avg} + \left[ m v_y^2 \right]_{avg} + \left[ m v_z^2 \right]_{avg} \\ &= \frac{1}{N} \sum_{i=1}^N m_i v_{i,x}^2 + \frac{1}{N} \sum_{i=1}^N m_i v_{i,y}^2 + \frac{1}{N} \sum_{i=1}^N m_i v_{i,z}^2 \\ &= \frac{1}{N} \sum_{i=1}^N (m_i v_{i,x}^2 + m_i v_{i,y}^2 + m_i v_{i,z}^2) \\ &= \frac{1}{N} \sum_{i=1}^N m_i (v_{i,x}^2 + v_{i,y}^2 + v_{i,z}^2) = \frac{1}{N} \sum_{i=1}^N m_i v_i^2 = \left[ m v^2 \right]_{avg} = 3k_B T \end{aligned}$$

- Now take the result here and define the *average* kinetic energy of the molecules:
- This is an extremely important result since it makes a connection between the *macroscopic* temperature and the *microscopic* average kinetic energy of the molecules
  - Temp. is a measure of the internal energy stored as kinetic energy of the molecules.

# Brownian Motion

- The relationships that we just derived apply to mixture of gases as well.
  - We did not depend on having the same mass for all objects...we did factor it out at one point, but we could always do the factorization in several different ways.
- Consider two gases in a single container that have established thermal equilibrium.

- Masses of molecules is  $m_1 < m_2$ .
- We then can make the following statement

$$\frac{1}{2} m_1 \left[ v_1^2 \right]_{avg} = \frac{3}{2} k_B T = \frac{1}{2} m_2 \left[ v_2^2 \right]_{avg}$$

- Examining this expression we see that the more massive molecule should have a lower speed, while the less massive molecule has a higher speed.
- We can estimate the *average speed* by solving for the *average squared speed* and then taking the square root.

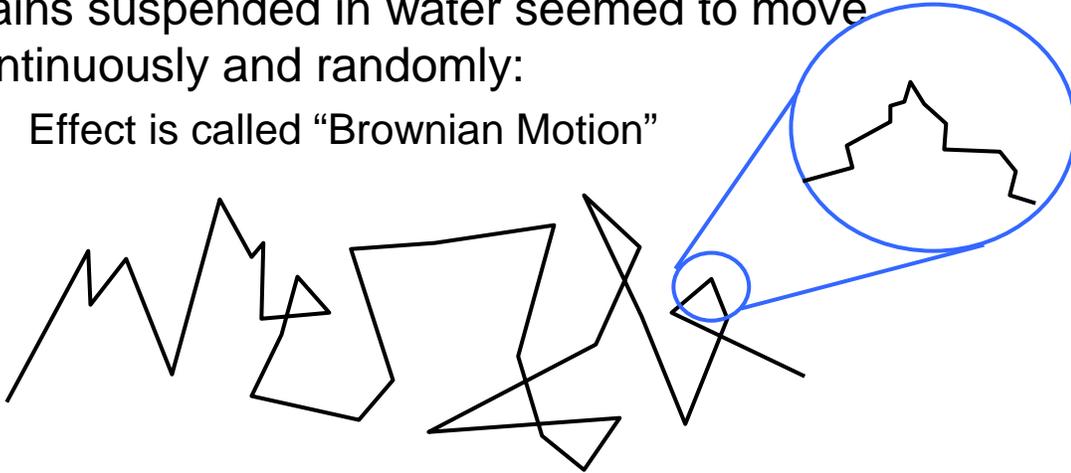
Ideal Gas Only

- This is not the exact *average speed* because we averaged the squares before taking the square root...but it is an approximation.
  - We call this the **root-mean-square (rms)**.
  - He at Room Temp:  $v_{rms} \sim 1360$  m/s
  - N at Room Temp:  $v_{rms} \sim 510$  m/s (recall  $v_{sound} \sim 343$  m/s)

# Brownian Motion

- In 1827, Robert Brown (Botanist) observed that pollen grains suspended in water seemed to move continuously and randomly:

- Effect is called “Brownian Motion”



- In 1905, Einstein showed that the motion could be explained in terms of the equality of the average Kinetic Energy of the pollen and the water molecules and that the motion was due to collisions between the pollen and the water molecules.
  - Einstein even showed that one could measure Avogadro's Number from these observations. (We won't go into it here.)
  - In 1908, Jean Perrin measured Avogadro's number using Brownian Motion...it earned him the 1926 Nobel Prize.
  - This provided additional evidence that atoms were real objects that were too small to see.
  - It help support Boltzmann's work in statistical mechanics...unfortunately this all came to light several years after Boltzmann committed suicide.

# Thermal Energy of a Gas

- With the expression for the average Kinetic Energy we can derive a simple expression for the internal energy of an **ideal** gas in terms of the temperature.
  - This was one of our goals!

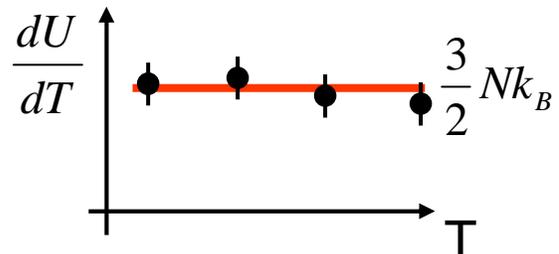
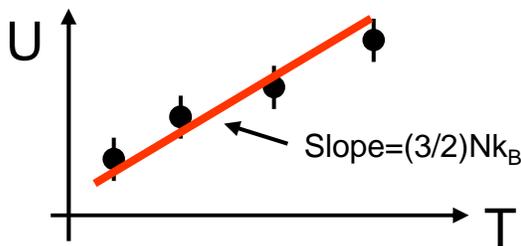
- Notice that this gives us an expression for how the temperature changes when we add energy to the gas.

$$\frac{dU}{dT} = \frac{3}{2} Nk_B$$

Recall From Unit C:

$$dU = mcdT \Rightarrow \frac{dU}{dT} = mc$$

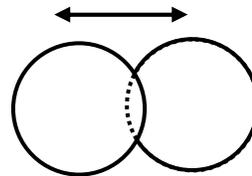
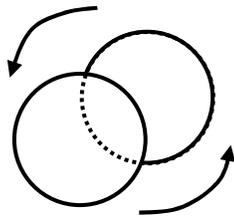
- Experimentally this is easy to test.
  - Get a sample of a known amount of gas.
  - Add a known amount of energy to it.
  - Measure how the temperature changes when we do this



- Does nature behave this way? After all, this prediction was based on our model of an ideal gas...this is still no guarantee that nature has to work this way.
  - For gases like He, Neon, Argon, Krypton, Xenon (all Noble gases) this seems to work fine.
  - For other gases it seems to fail.

# Thermal Energy

- What went wrong with our model for the other types of gases?
  - Noble Gases are *single* atom molecules (monatomic)
  - The other gases are diatomic ( $H_2$ ,  $N_2$ )
    -
  - Even other gases like water vapor have many atoms.
    -
  - There still seems to be multiples of  $Nk_B$ ! So there is still some structure.
- Our derivation of the total internal thermal energy depended on all the energy being in the kinetic energy of the molecules.
  - When the molecules are more complicated, it is possible to store energy in rotational and vibrational modes of the molecules.



- **NOTE: our statement that the temperature is related only to the average kinetic energy still holds! The energy in these other modes **does not** effect the temperature...it just means we have to dump more energy into the gas to get its temperature to go up.**

# Thermal Energy

- If you map out  $dU/dT$  as a function of  $T$  you see these other modes “switching on”



- Why?? (Later we will see why...we need to develop a few more concepts first!)
- It is interesting that the steps are always in units of  $Nk_B$
- We see that we have
  - Near Room Temp  $f = 3$  for monatomic gases,  $f = 5$  diatomic gases and  $f > 6$  for others.
  - Applies to real gases in the ideal gas limit (low density)
  - $f$  can go through step changes as we move up in temperature and “switch on” various rotational and vibrational modes. In between these steps there is a transitional stage.

# Examples

# Solids and Liquids

- We have constructed an interesting model for gases. Can we extend these ideas to solids and liquids?
  - In the case of solids and liquids we cannot use the model for an ideal gas.
    - The molecules are too close to one another and therefore their interactions become an important part of the model.
      - In the case of the solid the molecules are held locally by a lattice.
- Nonetheless there are a couple of simple qualitative features we can extrapolate to solids and liquids
  - Solid and liquids do store energy internally as both kinetic energy and vibrational energy (potential energy) of the molecules.
  - Liquids empirically store energy which is ~few times  $k_B T$  per molecule.
  - Many liquids also have an average kinetic energy that is  $(3/2)Nk_B T$ , just as with gases
  - By experimentally measuring  $dU/dT$  for solids, we find that
    - This is seems to be about 2 times that of a gas. **Is there a deeper meaning here?**
- We have come across more questions. What we need now is a (QM) model for solids...but first let's complete our work with gases.